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ROYAL CANADIAN MINT PILOT PLANT FOR SOLVENT EXTRACTION OF PLATINUM AND PALLADIUM

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by

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ABSTRACT

Pilot plant studies have been carried out on the treatment of spent gold electrolyte from the Royal Canadian Mint by solvent extraction to recover platinum and palladium values. A flowsheet for the extraction of Pt and Pd away from copper with selective and separate stripping of the two precious metals has been devised. The process shows promise as a novel technique for the recovery and separation of platinum and palladium from chloride solutions. Some additional work is required to solve problems with platinum stripping and fully develop the technology.

USINES EXPÉRIMENTALES DE LA MONNAIE ROYALE CANADIENNE POUR L'EXTRACTION DU PLATINE ET DU PALLADIUM

par

R. Molnar

RÉSUMÉ

Des essais à l'échelle-pilote ont été menés dans le but de traiter l'électrolyte d'or usé en provenance de la Monnaie royale canadienne. Ces essais consistaient dans l'extraction du cuivre par solvant en vue de récupérer le platine et le palladium. Un schéma de fonctionnement pour l'extraction du Pt et du Pd du cuivre par extraction sélective et individuelle a été élaboré. Le procédé offre des possibilités en tant que nouvelle technique de récupération et de séparation du platine et du palladium des solutions de chlorure. Des travaux de recherche additionnels sont nécessaires pour solutionner les problèmes relatifs à l'extraction du platine et du palladium et mettre la technique au point.

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INTRODUCTION

Work is being carried out at CANMET on novel technology for the recovery of precious metals from chloride liquors, specifically using solvent extraction. Bench scale work had identified a reagent which could extract platinum and palladium from strong chloride solutions. The next step in the work was to be small scale pilot plant testing. However, problems were being encountered because of the cost of making up sufficient synthetic solution to operate the pilot plant for a useful length of time.

The Royal Mint in Ottawa operates a gold refinery. They produce, from their gold electro-refining circuit, a spent chloride electrolyte which contains principally; gold, platinum, palladium and copper. The gold is precipitated with SO_2 and the platinum and palladium are presently isolated by ion exchange. The ion exchange step is costly because the loaded resin has to be burned and the ash sold for further recovery of the metal values. The Mint has been looking for ways to replace the ion exchange step to enable them to recover a more valuable product at lower cost.

It was decided in discussions between the Mint and CANMET that collaboration would be beneficial to both parties. CANMET could carry out pilot plant work at the Mint to further their research using real solutions. This work would also be of interest to the Mint in their search for an alternative to the ion exchange step.

The Mint solutions contain approximately 10 g/L copper. Precipitation of platinum and palladium by sodium formate is the technique being investigated by the Mint because it yields a high purity metal product. However, the copper which is present in greater amounts than Pt and Pd interferes with the precipitation process and results in the loss of precious metal values. The objective of this work was to use the technology developed on a bench scale at CANMET which enabled the extraction of Pt and Pd away from the Cu with selective stripping of these metals to yield two relatively pure products by precipitation. The Cu could then be recovered by cementation. The selective extraction of copper was also considered and is discussed separately.[1]

EXTRACTION OF PLATINUM AND PALLADIUM

Background

The proposed flowsheet which was to be tested for the eventual production of three separate product streams is illustrated in Fig. 1. The design of the circuit is based on work which has been carried out at CANMET and is being continued by CANMET and McGill University.[2,3] It essentially involves the use of solvent extraction to co-extract Pt and Pd away from the copper. These metals are then selectively stripped using water for Pt and strong acid for Pd. The objectives of pilot plant testing were to confirm the bench scale design data and to identify any areas of potential difficulties.

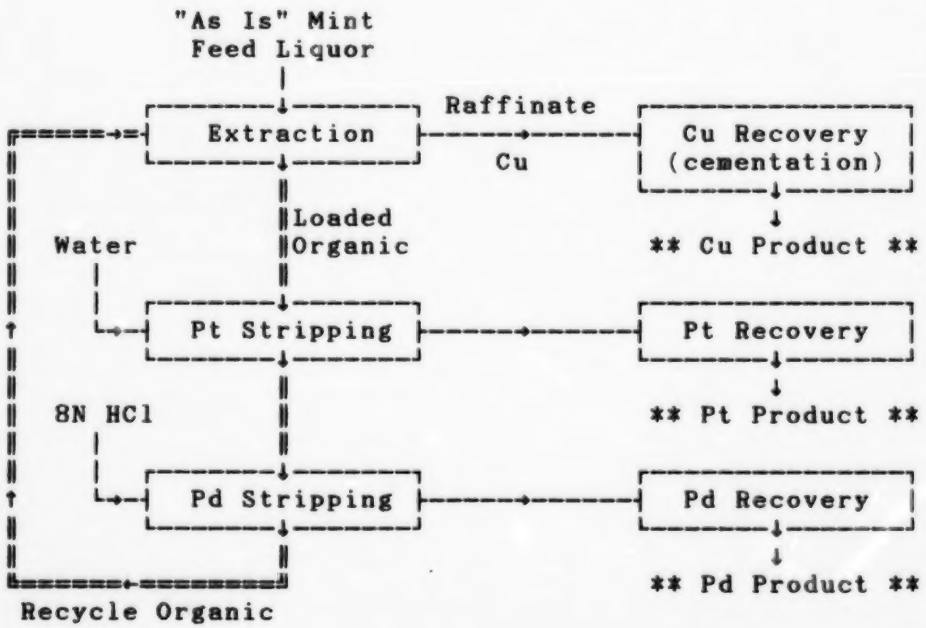


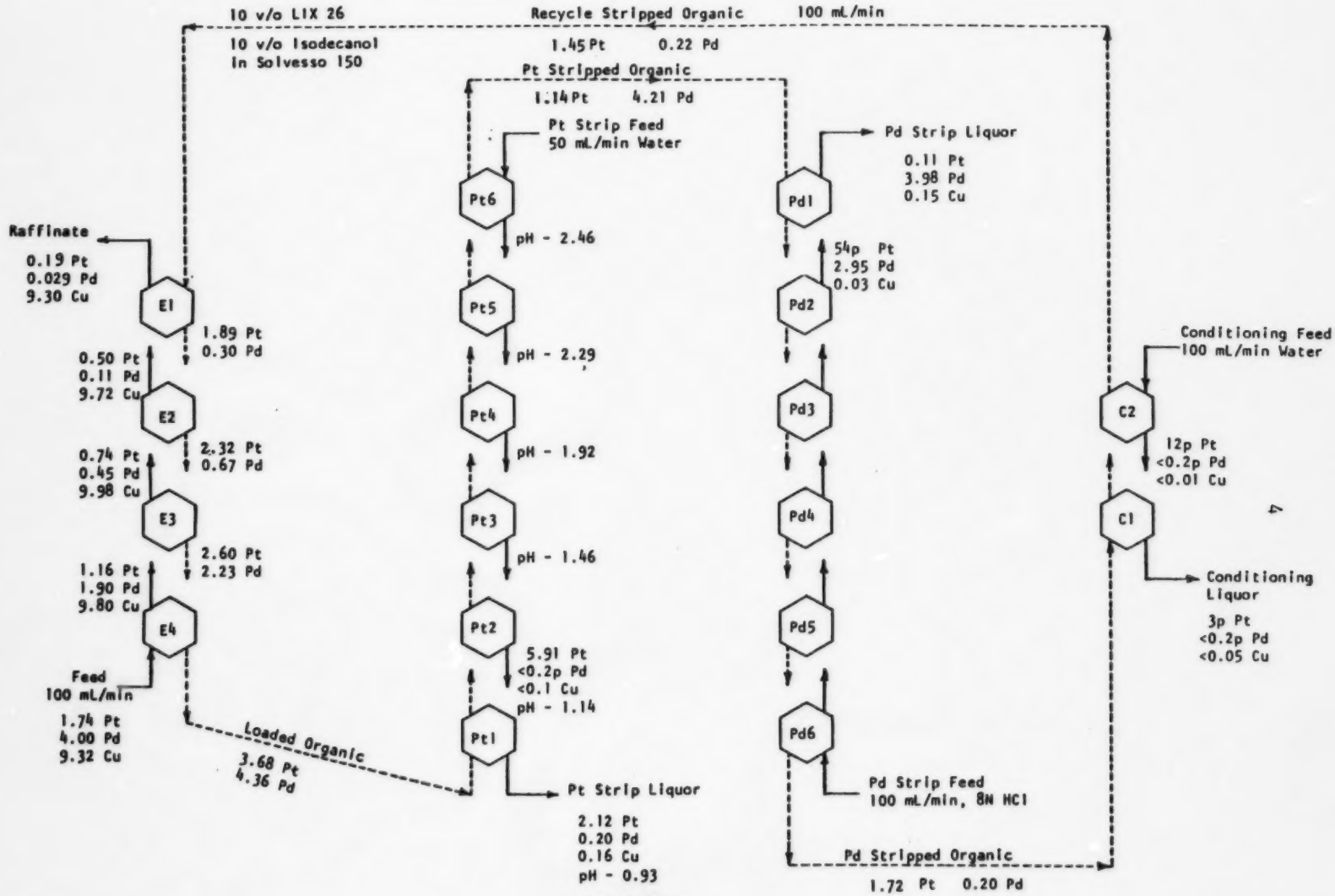
Figure 1. Proposed Flowsheet for Mint Liquor Treatment

Experimental

The pilot plant was carried out in the Mint. Bell Engineering type laboratory mixer-settlers were used for all the stages. The organic mixture selected was 10 v/o LIX 26 (Henkel Ltd.) with 10 v/o isodecanol modifier dissolved in Solvesso 150 (Exxon). The modifier was necessary to prevent the formation of a third phase between the organic and aqueous. Samples were taken periodically as conditions were altered and these were all analysed at CANMET for metal content using atomic absorption spectrophotometry.

The feed solution to solvent extraction contained, in g/L, 1.74 Pt, 4.00 Pd, 9.32 Cu and about 100 HCl. This was to be contacted with the organic. Platinum was to be selectively recovered from the loaded organic by stripping with water while palladium could be stripped with 8 N HCl. In all steps of the circuit, the organic and aqueous flows were counter-current. No special measures were taken to control the continuous phase, but because of the inherent nature of the equipment, it can be safely assumed that aqueous continuous conditions were operated throughout the circuit.

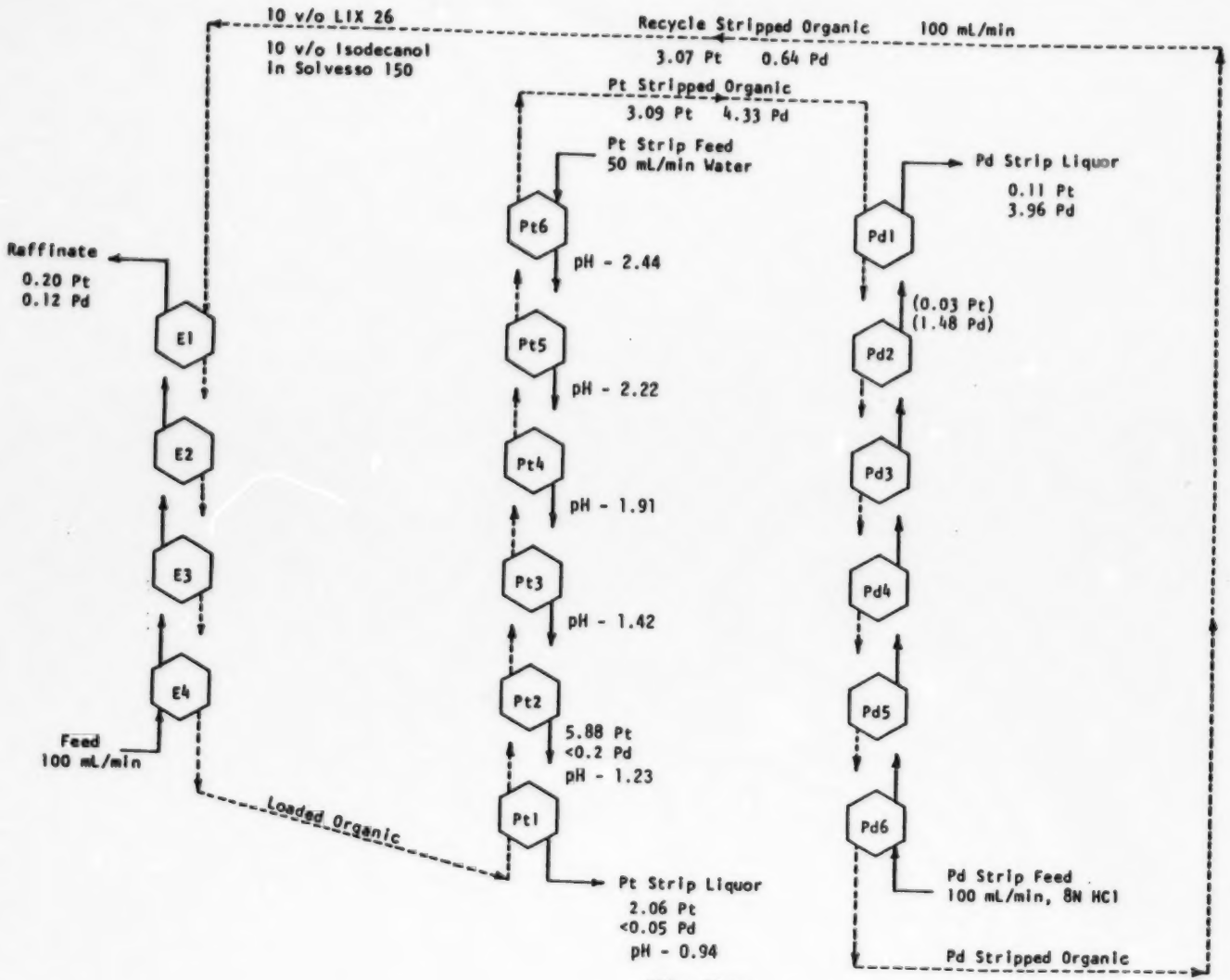
The initial arrangement tested is shown in Fig. 2. The conditions were determined from equilibrium isotherms and other data developed at CANMET.[2] Four extraction stages were followed by six stages to strip platinum. The palladium was next stripped in six stages and the organic was passed through two stages of tap water conditioning before being recycled to extraction to complete the circuit. The water conditioning was added because it was thought that the strong acid contact from Pd stripping might inhibit extraction. Water conditioning was removed after 10 hours of operation as Fig. 3 shows. After 14 hours of operation, the order of Pt and Pd stripping was switched (Fig. 4), and after 18 hours, the strength of the Pd strip feed was reduced to 5N HCl from the initial 8N (Fig. 5). The operation was terminated after 22 hours. Table 1 summarizes the phase ratios used, the flow rates and the mixer and settler residence times.



Pilot Plant
RCMP-1
Room Temperature, Organic Recycle, Bell Cells

All concentrations in g/L except p = ppm,
10 hrs operation.

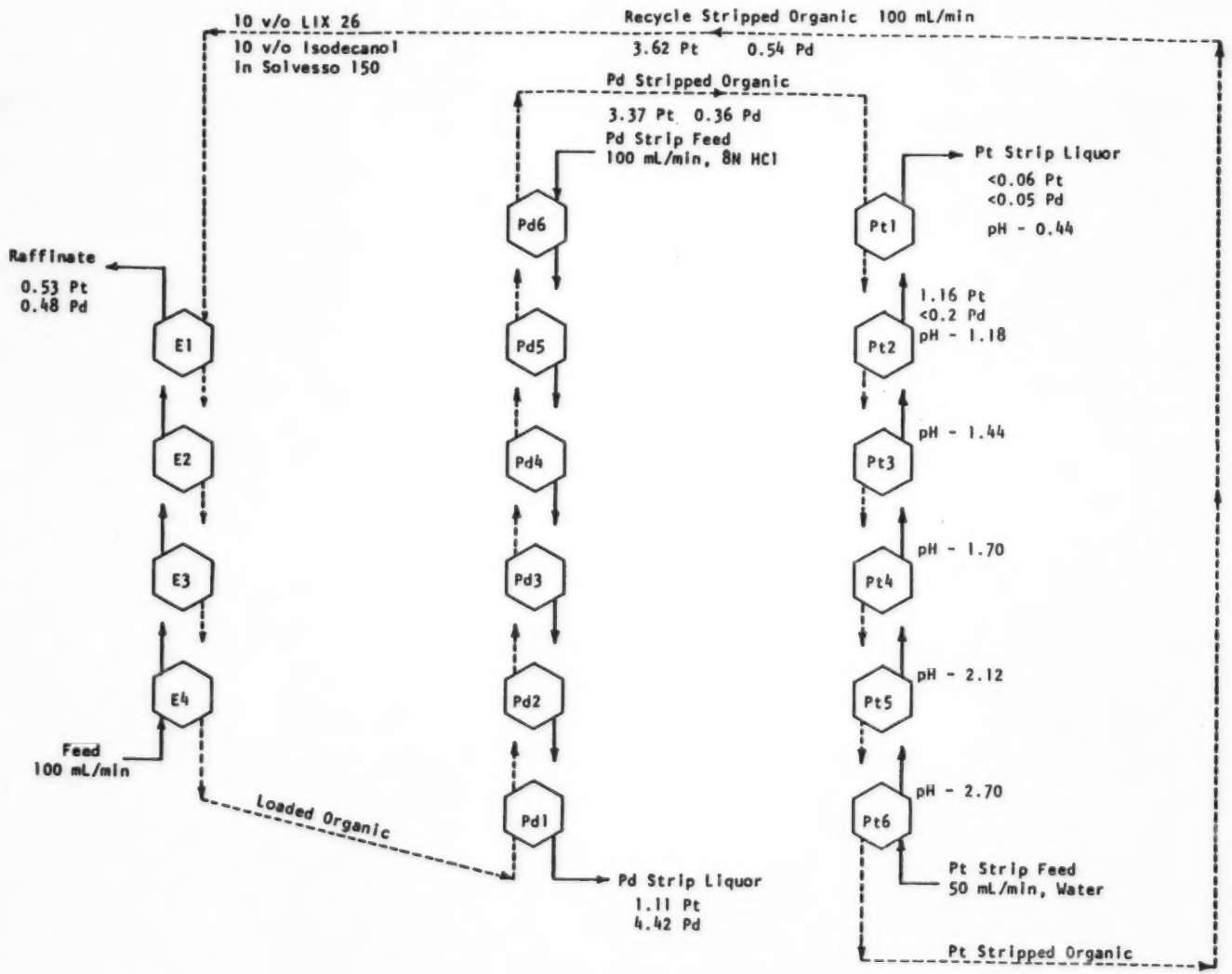
Figure 2. Pilot Plant Results, 10 hours



Pilot Plant
RCHP-1
Room Temperature, Organic Recycle, Bell Cells

All concentrations in g/L except p = ppm,
14 hrs operation, 4 hrs since conditioning removed
Values in ( ) at 12 hrs operation

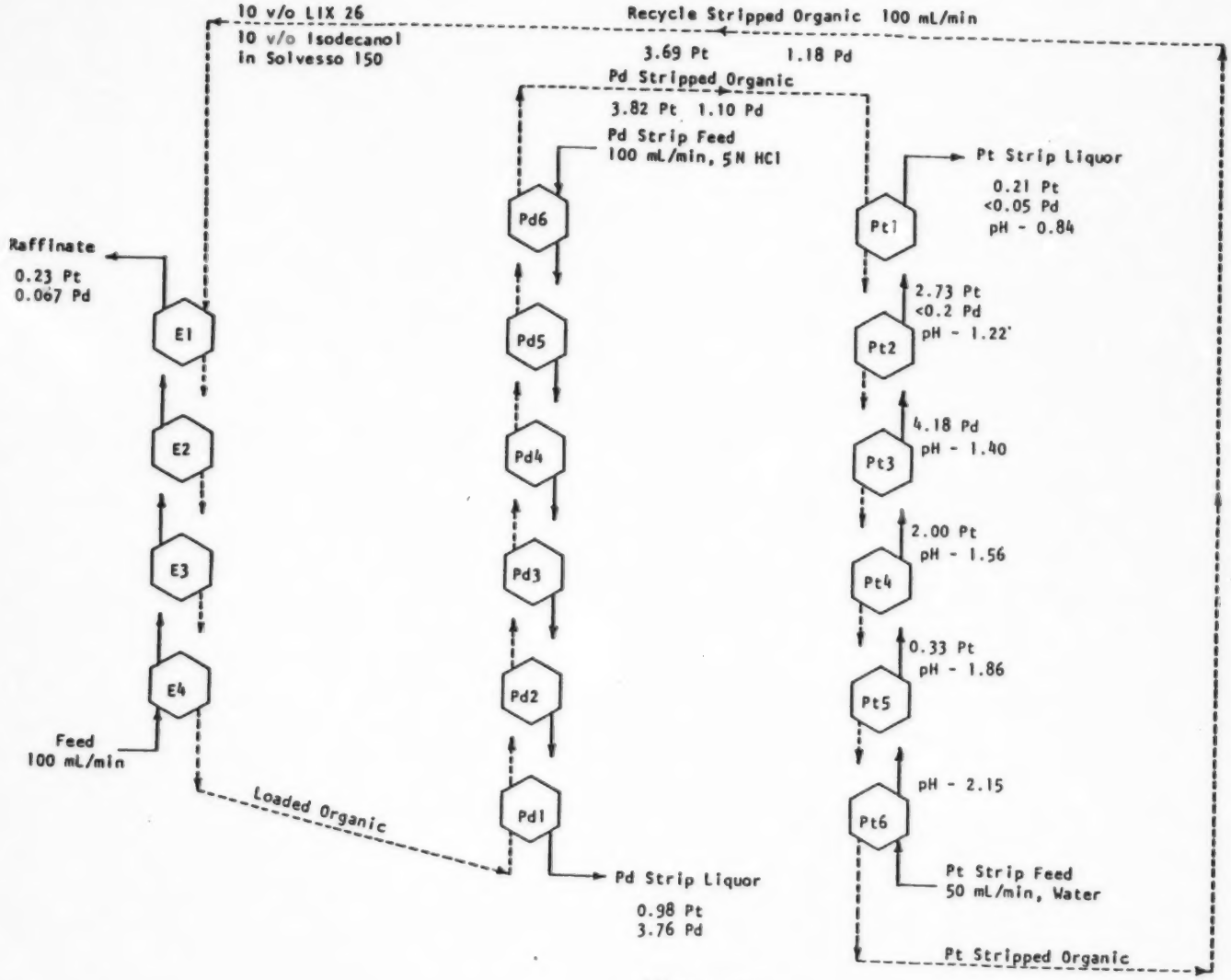
Figure 3. Pilot Plant Results, 14 hours



Pilot Plant
RCHP-1
Room Temperature, Organic Recycle, Bell Cells

All concentrations in g/L except p = ppm,
18 hrs operation, 4 hrs since reversal of
stripping order

Figure 4. Pilot Plant Results, 18 hours



Pilot Plant
RCMP-1
Room Temperature, Organic Recycle, Bell Cells

All concentrations in g/L except p = ppm,
22 hrs operation, 4 hrs since change to 5N stripping.

Figure 5. Pilot Plant Results, 22 hours

Table 1. Operating Conditions

Parameter	Extraction	Pt Strip	Pd Strip	Conditioning
Phase Ratio O/A	1	2	1	1
Flows O/A mL/min	100/100	100/50	100/100	100/100
Res t mixers min	3.1	4.1	3.1	3.1
Res t settlers min	3.9	4.8	3.9	3.9

Room temperature

RESULTS AND DISCUSSION

With approximately 18 L of organic in the system it could be estimated that the organic would cycle through the circuit in about 3 hours. After the initial 10 hours at one condition, operating parameters were altered every four hours. When the conditioning stages were removed, the organic inventory was reduced by 1.5 L and the cycle time was correspondingly reduced. It was assumed that the system had substantially come to equilibrium after the first 10 hours. The removal of conditioning stages had little effect on the circuit so equilibrium was quickly re-established. The alteration of the stripping order was a major change and it took some time for the system to settle down again physically and therefore chemically. However, the change to 5N acid had only a small effect on the operation so it is safe to say that the system was operated for about 8 hours, or again roughly three organic cycles after the major change in conditions had been made at 14 hours.

The physical operation of the extraction stages was satisfactory. Both phases were clear and separated well. A small amount of interfacial emulsion built up in the cells, with the majority in E1. This emulsion layer which varied between 1-2 cm (out of an 8 cm total settler depth) throughout the run concentrated down to a small crud layer upon standing overnight. There was not enough material to collect for identification.

In the Pd stripping circuit, operation was also stable throughout the run. Both phases again separated clearly but the separation was slower and a dispersion band of 3-5 cm thickness was noted in each stage. Upon standing, this cleared completely with no crud formation. Changing the order of stripping and changing the strength of the strip feed did not affect the physical operation of the Pd stripping stages.

The Pt stripping circuit was difficult to operate and needed constant attention. There was a tendency for the accumulation of emulsions in the settlers to the point where the settlers would be flooded, particularly in cells Pt4 to Pt6. However, it was possible to get clear solutions with sufficient settling time. Some precipitation was also noted in the stages with the emulsion problems. When the order of stripping was changed, the emulsion problem decreased but there was a stable crud layer of 1-2 cm formed in cells Pt5 and Pt6. Organic contacts with water often lead to emulsion difficulties and therefore the problems encountered, particularly at the aqueous feed end of the Pt strip section, were not unexpected.

The conditioning circuit suffered from the same problems as the Pt strip circuit. There was a tendency for emulsion build-ups which flooded the settlers upsetting operation. A small amount of precipitation was also noted. The main reason for the removal of the conditioning stages was because there seemed to be little need for them inasmuch as the feed water pH was not substantially different from the final liquor pH. This indicated that the organic phase did not carry a great deal of acid. Furthermore, once the stripping order was reversed, there was no need for conditioning stages because Pt stripping was also a water wash. The conditioning step was an unnecessary complication of the circuit.

Figures 2 to 5 contain the results of all the chemical analyses carried out on the samples taken during the operation. An examination of these results enables the following observations to be made, namely:

- platinum was not being effectively stripped.
- only small amounts of platinum were lost in the conditioning.
- the extraction of platinum and palladium worsened progressively until the last set of samples taken after the order of stripping had been reversed.
- reduction in the strip feed strength from 8N to 5N HCl slightly reduced the strip liquor concentration.
- Pd was recovered satisfactorily. However, when Pd was stripped before Pt, there was some co-stripping of the Pt decreasing product purity.
- there was some co-extraction of copper which was stripped in the first stripping stages.

The most important problem encountered in the circuit was the poor platinum stripping. It was observed that the Pt content of the aqueous phase in the Pt2 cell was double that in the strip liquor. What seems to be taking place is that acid is being carried out of the extraction circuit by the loaded organic. It is known that some small amount of acid will be extracted by the LIX 26. Pt extraction is very sensitive to acid level. The loaded organic contacts aqueous from Pt2 in the first strip stage (Pt1) and the acid is rapidly washed from the organic. The organic is now in contact with a mildly acidic aqueous phase which favours Pt extraction and complete stripping of Pt is not possible. In Pt2 the Pt is stripped because the organic has no more loaded acid to acidify the aqueous with. However, the Pt level in the whole stripping circuit backs up until only a portion can be stripped off, and consequently the Pt stripped organic still contains a substantial amount of Pt. The Pd circuit is able to strip off a small amount of this leftover Pt. The proportion increases as the Pt left increases with successive cycles of the organic. This contaminates the Pd strip liquor and decreases Pd stripping capacity. Therefore, both Pt and Pd build up on the organic with each cycle as is clearly seen in the results. On each pass there are less sites available on the organic to extract Pt and Pd from the feed and so extraction efficiency decreases as seen from the steadily increasing values of Pt and Pd in the raffinates.

The results show that changing the order of stripping was not advantageous. Some Pt is stripped, even with the stronger 8N acid. However, the early results indicated that Pt is very selectively recovered as long as no acid is present so it makes more sense to strip Pt and then send the Pt free organic to Pd recovery.

CONCLUSIONS AND RECOMMENDATIONS

The major conclusions drawn from the single pilot plant campaign are that:

- with effective stripping of the organic, good extraction can be obtained. It may be necessary to use one more stage to lower the raffinate to desired levels.

- Pt is more selectively stripped than Pd and therefore should be stripped first in order to recover the purest product streams.
- a conditioning stage to remove acid from the recycle organic is not required.

Further work needs to be carried out to resolve the Pt stripping problems. A number of possible avenues of inquiry are available. Control of the pH in the Pt stripping circuit by the addition of base between the stages is possible provided that certain difficulties are avoided. Addition of dilute base solution may dilute the strip liquor excessively. On the other hand, the use of concentrated base may result in local precipitation of metals which can cause emulsion problems. Preliminary work now being carried out at CANMET[4] has indicated that it may be possible to do a controlled neutralization without running into precipitation or excessive dilution problems.

It may also be possible to scrub the organic phase with a bleed of Pt strip liquor. This way, the acid could be selectively removed before stripping. It is not necessary to remove all the acid off the organic but just enough to prevent the acidification of the strip liquor below the pH 1.2-1.3 range. The acid content of the loaded organic is in equilibrium with the feed acid of about 3N. This acid content is about 0.06N estimated from the pH of the strip liquor where the acid reports. Reducing the acid content of the organic to 0.015N (scrubbing 0.045N) would give a strip liquor pH of around 1.5 if all the remaining acid comes off in the strip liquor. This would not inhibit Pt stripping. An organic with 0.015N acid would be in equilibrium with an aqueous of about 0.7N. Scrubbing could be carried out at around O/A = 15/1 (estimating that - capacity of scrub liquor to maintain equilibrium with desired organic/amount of acid which has to be removed to reach desired level = 0.7/0.045 = 15).

In summary it can be stated that the co-extraction of Pt and Pd seems to be a practical and useful technological advance in the separate recovery of precious metals from mixed solutions. The results of this preliminary pilot plant show that the proposed process is feasible. Some further work is required to overcome some small process problems in order to optimize the operation of the solvent extraction circuit.

ACKNOWLEDGEMENTS

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